SEPARATOR DEVELOPMENT
FOR A HEAT STERILIZABLE BATTERY
Quarterly Summary Progress Report 1

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ABSTRACT

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Several ligand-containing vinyl polymer systems were selected for evaluation as battery separator materials that would be usable in heat sterilizable Ag-Zn batteries. These ligand polymers are prepared by two general procedures: (1) copolymerization of vinyl ligand monomers to form polymers having bidentate chelate functionality, and (2) direct substitution of ligand groups on a preexisting polymer backbone. Of the 28 polymers tested for stability in 40% KOH at 135°C thus far, several types have shown high resistance to degradation by 40% KOH at 135°C after 60 hours exposure. The most promising materials were copolymers of 2-vinylpyridine with either acrylic or methacrylic acid, and polymers containing ligand groups substituted on a polystyrene backbone through a methylene group. Polymers that show high stability in 40% KOH in our first phase tests are now being made into membranes for comprehensive evaluation as battery separators. Initial tests indicate that membranes prepared by the *in situ* saponification of 2-vinylpyridine-methyl acrylate copolymers have both acceptable electrical resistances ($\sim$ 100 ohm-cm) and usable mechanical toughness.

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I. INTRODUCTION

The primary objective of this program is the development of battery separator materials that will function satisfactorily in a sealed Ag-Zn secondary battery following heat sterilization at 135°C. This separator material should have the following characteristics:

1. High adsorption of electrolyte and wettability.
2. Low electrical resistivity.
3. Low permeability for Ag and Zn complex ions in the electrolyte.
4. Good chemical stability in 40% KOH containing dissolved silver ion species at 135°C.
5. Mechanical strength and flexibility at ambient temperature and at 135°C in 40% KOH.

Several types of ligand-containing vinyl polymers have been selected as candidates for this purpose. These polymers have the unique ability to restrict metal ion migration in the cell by chelation of these ions in the form of olated complexes.

Our program has been divided into the following four phases:

1. Preparation of model ligand-containing polymers.
2. Screening of the model polymers for thermal stability at 135°C and for hydrolytic stability in 40% KOH at 135°C.
3. Preparation of copolymers and membranes using polymer units that showed high stability in our screening test.
4. Comprehensive evaluation of our best membranes as battery separators.

During this first report period, our specific objectives were to:

1. Prepare ligand-containing polymers by substitution of ligand groups on polystyrene and by copolymerization of monomers that form a ligand group in a 1:1 copolymer.
2. Screen these ligand polymers for thermal stability at 135°C and for stability in 40% KOH at 135°C.
3. Start preparation of copolymer systems based on units found to have the required stability in the screening tests.

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II. SUMMARY

Several types of ligand-containing vinyl polymers have been selected for development as heat sterilizable Ag-Zn battery separators. These polymers have the ability to restrict metal ion migration in the cell by chelation of these ions as olated complexes.

The following two general methods have been used to prepare the ligand-containing polymers: (1) Direct substitution of ligand groups onto an existing polymer backbone such as poly-styrene. This method is the most versatile in that a large selection of ligands can be incorporated into polymers by relatively simple synthetic procedures. However, we have found that in many cases a minor amount of crosslinking occurs as a side reaction, rendering the polymer insoluble and intractable for our purposes. Most success with this method has been in substitution of ligands on polystyrene through a methylene linkage.

The second method of preparation of ligand-containing polymers involves copolymerization of two vinyl ligand monomers to form chelating groups along the vinyl polymer chain. Good control of product composition is obtained using this method.

In the first part of our program 28 polymers were tested for their thermal and hydrolytic stability in 40% KOH at 135°C. The extent of any degradation that occurred in these tests was determined by a comparison of the sample weight, infrared spectra, softening point, solubility and specific viscosity of the polymers before and after exposure. The major conclusions that can be drawn from these tests are as follows:

1. 2-Vinylpyridine acrylic acid and 2-vinylpyridine methacrylic acid copolymers are highly resistant to 40% KOH at 135°C. These types of copolymers are of prime interest to this program because of their efficient chelation sites and because they are extremely hydrophilic. More comprehensive evaluation of these polymers as separator materials has started.

2. Several polymers containing ligand groups substituted on polystyrene through a methylene linkage showed good stability. Further testing of these polymers with catechol and 2-pyridylmethylamine substituents is planned.

3. Copolymers containing maleic anhydride units appear to have the required stability when in a polymer that is insoluble in 40% KOH. Styrene-maleic anhydride is being evaluated more extensively.

4. The nitrile groups in styrene-acrylonitrile copolymers resist hydrolysis, but a minor amount of ammonia was produced during exposure.

5. Amino and sulfonic acid substituents on polystyrene are stable, but nitro substituents rapidly degrade.

6. The stability of polyacetals derived from poly(vinyl alcohol) appears to be limited by their hydroxyl content, and they do not have sufficient stability for this application.

7. Poly(N-vinylimidazole) rapidly degrades in 40% KOH at 135°C.

The results of these tests are being used in two ways. First, we are preparing membranes from the polymer systems that showed high stability in our screening test and comprehensively evaluating these membranes. In this work our initial tests indicate that films made by the saponification of a 2-vinylpyridine-methyl acrylate copolymer and by the hydrolysis of a styrene-maleic anhydride copolymer in 40% KOH have acceptable resistivity and usable mechanical strength. Our screening test results are also being used to design copolymer systems having potentially improved battery separator properties on those presently being studied.

III. DISCUSSION OF RESULTS

A. SYNTHESIS OF LIGAND-CONTAINING POLYMERS

1. General

Two general methods were used to prepare the ligand-polymers. One method involved substitution of ligands on a polymer backbone by a coupling reaction. This method was used to substitute ligands on polystyrene via methylene, azo, or amino linkages. Polymers prepared by this method are described in Section III.A.2 of this report.

A limited amount of work was also done using this method to substitute ligands on poly(vinyl alcohol) by reaction with ligands containing aldehyde substituents to form an acetal polymer. This work was terminated when the results of our stability tests of these acetal polymers in 40% KOH showed that they did not have the required stability for this application.

The second method used to prepare ligand-polymers was by the copolymerization of two ligand monomers to form a chelate group directly in the 1:1 copolymer. Polymers that were prepared by this method are described in Section III.A.3.

The ligand groups of primary interest for incorporation into these polymers are given in Table 1. These particular chelating groups were chosen for the following two reasons. First, they form stable chelates in basic media. Second, they should have good stability in strong caustic at 135°C.

2. Substitution of Ligands on Polystyrene
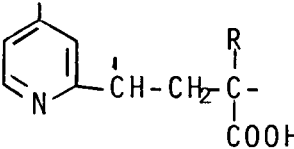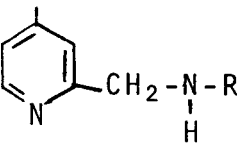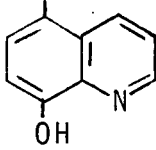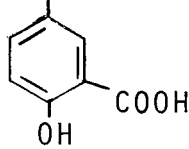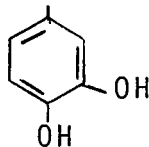
a. Through a Methylene Linkage

Ligands were substituted on polystyrene through the methylene group by reactions of these ligands with chloromethylated linear polystyrene. This intermediate was prepared by chloromethylation of a 1% solution of polystyrene in dichloroethane with chloromethylmethylether and a stannic chloride catalyst. The procedure used was that of Gregor and coworkers (ref. 1) except that we found it necessary to use high dilution for reactions involving high molecular weight polystyrene (ca. 100,000) in order to maintain sufficient solubility of the product and to prevent by-product crosslinking. Polymers prepared by this method had approximately 40% chloromethyl substitution.

Two reaction sequences with polyvinylbenzylchloride were used for substitution of the ligands. The first method involved the reaction of the polymer with reactive amino-substituted ligands. This route is illustrated in the preparation of poly-

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Table 1

LIGAND GROUPS FOR INCORPORATION INTO VINYL POLYMERS

Name	Structure	Donor Groups	
1. Pyridine-acids		N	O
2. Aminopyridines		N	N
3. 8-Hydroxyquinolines		N	O
4. Salicylic Acid		O	O
5. Catechol		O	O

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vinylbenzyl-2-(2-pyridylethyl)amine.

$$\left[\begin{array}{c} -CH-CH_2- \\ \\ \\ CH_2Cl \end{array}\right]_n + \quad \text{(pyridyl)} CH_2-CH_2-NH_2 \longrightarrow \left[\begin{array}{c} -CH-CH_2- \\ \\ CH_2 \\ NH(CH_2)_2\text{(pyridyl)} \end{array}\right]_n$$
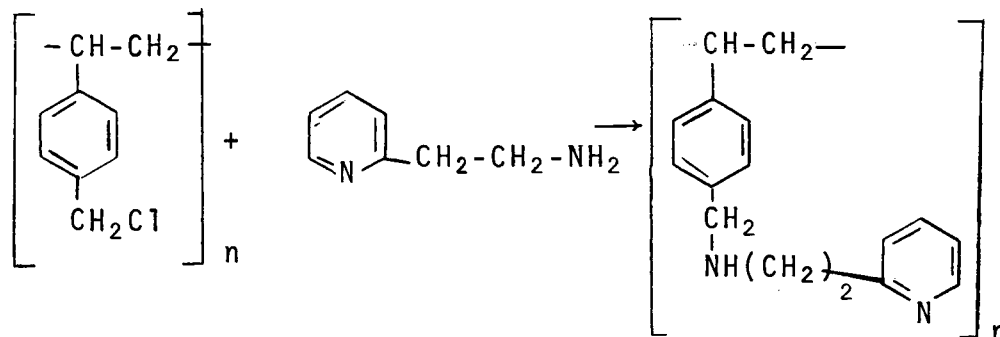
Other ligand-containing polymers prepared by this route were polyvinylbenzyl-2-pyridylmethylamine and polyvinylbenzyl-1-(β-aminoethyl)-2-methyl-2-imidazoline.

The amino groups on 5-aminosalicylic acid and 5-t-butylamino-methyl-8-hydroxyquinoline were unreactive and did not yield the desired products. With the t-butylaminomethyl group on 8-hydroxy-quinoline, steric hindrance probably caused the observed low reactivity. Attempts were made to prepare the n-butyl-substituted compound. However, reaction of 5-chloromethyl-8-hydroxyquinoline hydrochloride with excess n-butylamine yielded only disubstituted product:

$$\text{(8-hydroxyquinoline-5-CH}_2\text{Cl)} \cdot HCl \quad + \quad C_4H_9NH_2 \longrightarrow \left(\text{(8-hydroxyquinolin-5-yl)}CH_2-N\right)_2-C_4H_9$$
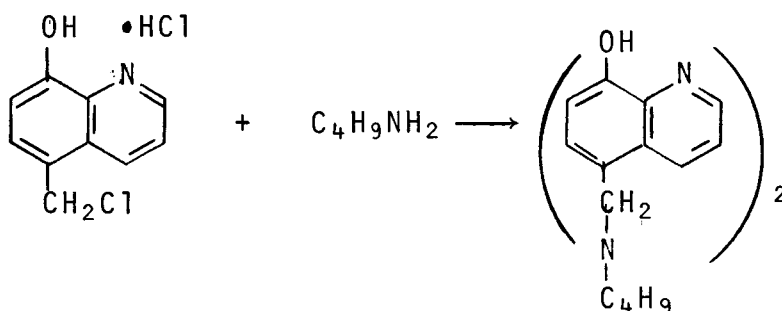
The Friedel-Crafts reaction was the second method used for reaction of ligands with polyvinylbenzylchloride. Polyvinyl-benzylcatechol and polyvinylbenzylsalicylic acid were prepared by this route using reaction conditions developed by Kun (ref. 2) for substitution of hydroquinone on polystyrene.

$$\left[\begin{array}{c} -CH-CH_2- \\ \\ CH_2Cl \end{array}\right]_n + \quad \text{(catechol, OH, OH)} \quad \xrightarrow{ZnCl_2} \quad \left[\begin{array}{c} -CH-CH_2- \\ \\ CH_2 \\ \text{(ring, OH, OH)} \end{array}\right]_n$$

Polyvinylbenzylcatechol

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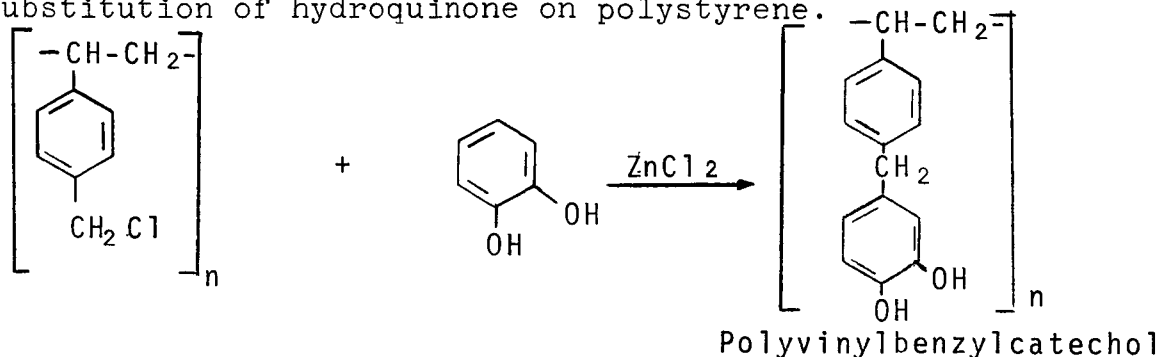
b. Through an Azo Linkage

The ligands, 8-hydroxyquinoline and salicylic acid, were substituted on the polystyrene backbond through an azo linkage using a reaction sequence developed by Davies and co-workers (ref. 3). This reaction sequence involves the following four steps:

(1) Nitration of polystyrene to form poly (p-nitrostyrene).

(2) Reduction of the nitro groups with stannous chloride in HCl to give poly (p-aminostyrene).

(3) Diazotization of the amino groups, and

(4) Reaction of the diazonium compound with the ligand in a basic medium at 0-5°C.

Substitution of the ligand at the azo linkage occurs *para* to the ligand hydroxyl groups.

The products prepared by this sequence from linear, high molecular weight polystyrene were not pure azo-substituted linear polymers but contained free nitro functions. These polymers were infusible at 300°C and practically insoluble in all organic solvents. It is possible to eliminate the nitro group impurities present by using a modified reaction sequence employing the method of Zenftman (ref. 4) for nitration of polystyrene. However, because of the poor mechanical properties of these polymers, no further work is planned with them.

c. Through an Amino Linkage

Pyrimidine was substituted on polystyrene (through an amino group) by reaction of 2-chloropyrimidine with poly(aminostyrene) in pyridine to give a ligand substituent with NH and N donor groups.
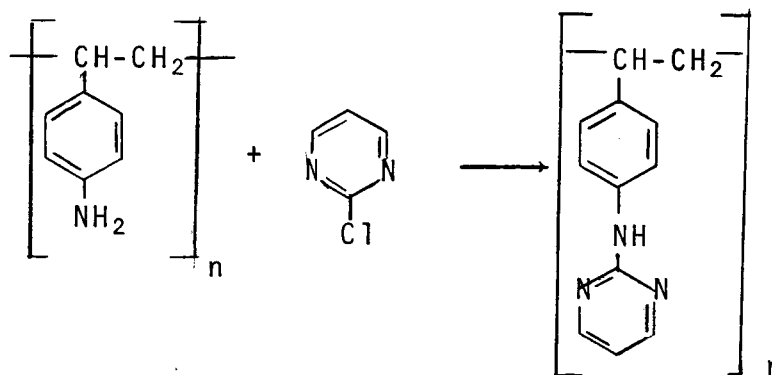
The poly(aminostyrene) used in this preparation was prepared by the modified reaction sequence described above and was free of nitro groups.

3. Preparation of Copolymers

Chelation sites were introduced directly into a polymer by copolymerization of two ligand monomers that form a chelating site in each 1:1 copolymer unit. For example, copolymerization of 2-vinylpyridine and methacrylic acid yields a polymer with this ligand grouping:

$$\left[\overset{}{\underset{N}{\bigcirc}} -CH-CH_2-\overset{CH_3}{\underset{COOH}{\overset{|}{C}}}-CH_2 \right]_n$$
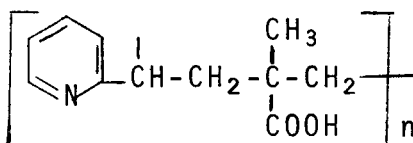
This copolymer was prepared by bulk polymerization of equimolar amounts of the above reactants with azo-bis-isobutyronitrile catalyst following a procedure described by Alfrey and Morawetz (refs. 5,6). This product polymer contained 0.57:0.43 ratio of 2-vinylpyridine to methacrylic acid. Data describing other polymers of this type that were prepared are in Table 2.

This type of polymer was among the most stable tested in 40% KOH in the screening program. However, both the above polymer and a polymer with a lower acid content (0.78:0.22) formed very brittle films. To overcome this difficulty we are now preparing the following three types of polymers, which should have superior mechanical toughness:

1. Terpolymers derived from 2-vinylpyridine, acrylic or methacrylic acid, and a flexible monomer such as butyl vinyl ether.

2. Copolymers of 2-vinylpyridine and methyl methacrylate or methyl acrylate that can be hydrolyzed *in situ* in a film to form the desired ligand-polymer while retaining film strength.

3. Terpolymers of maleic anhydride, 2-vinyl-pyridine, and a flexible ligand.

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Table 2

PROPERTIES OF POLYMERS CONTAINING 2-VINYLPYRIDINE

Ref.	Monomers†	Mole Ratio Monomers	Reaction Time(hr) at 60°C	Conversion wt-%	Solvent/ non-solvent Used for Purification	Mole Ratio Monomers in Polymer††
89765	2-VP: Methyl acrylate	0.33:0.67	4-1/3		benzene/hexane	0.56:0.44
89728	2-VP: Methacrylic acid	0.50:0.50	6(70°C)	13	methanol-benzene/ acetone	0.58:0.42
89794	2-VP: Methacrylic acid	0.60:0.40	4(70°C)	34	-/acetone	0.57:0.43
89795	2-VP: Methacrylic acid	0.67:0.33	4(70°C)	43	-/acetone	0.78:0.22
89787A	Ethyl-2-VP: Methacrylic acid	0.50:0.50	6(70°C)	8	-/acetone	0.58:0.42
94503	2-VP: Methylmethacrylate	0.50:0.50	7	16	benzene/hexane	0.54:0.46
94505	2-VP: Methylmethacrylate	0.30:0.70	7	20	benzene/hexane	0.38:0.62
94509	2-VP: Methacrylic acid: butyl vinyl ether	0.25:0.50:0.25	21*	20	benzene-methanol/ hexane and acetone/ hexane	0.35:0.55:0.10

† 2-VP is 2-vinylpyridine

†† Based on elemental analysis

* Temperature reached 132°C for about 15 min. last hour

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Polymers of the first two types have been prepared (Table 2). The polymers containing the ester groups give very flexible films, and one sample film of a 2-vinylpyridine-methyl acrylate co-polymer was successfully hydrolyzed in 40% KOH in a Teflon holder that preserved film shape during hydrolysis.

4. Preparation of Monomer-Ligands

A pyridine-acid ligand group with a 7-membered ring can be incorporated into a polymer via 2-pyridylacrylic acid. This monomer does not homopolymerize, but is known to copolymize with acrylonitrile (ref. 7). A sample of 2-pyridylacrylic acid has been prepared by reaction of 2-pyridine aldehyde with malonic acid using a procedure described by Marvel et al (ref. 7). This monomer is presently being polymerized with acrylonitrile. Because of the adverse effect on the silver electrode of ammonia formed by hydrolysis of nitrile groups in 40% KOH, the nitrile groups on this polymer will be hydrolyzed before testing.

We are also attempting to prepare the ligand-monomer, 2-vinyl-6-aminopyridine, by following the reaction sequence described by Cislak (ref. 8).
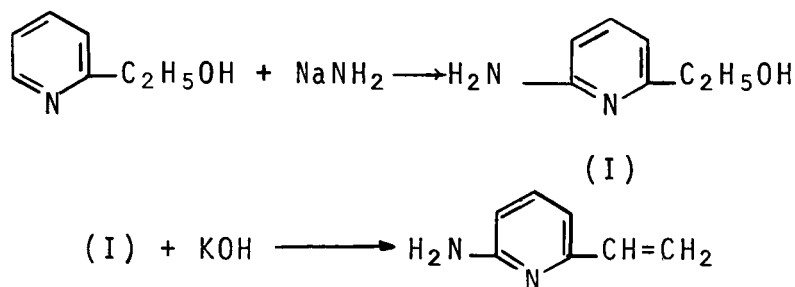
Initial attempts to prepare the intermediate, 2-amino-6-ethanol-pyridine (I), yielded only polymeric products together with distillable products that contained neither amino nor hydroxyl substituents. We will repeat preparation of this intermediate using dimethylaniline as solvent in place of xylene since this solvent reportedly improves yields in the amination reaction (ref. 9).

B. SCREENING TESTS FOR POLYMER STABILITY

1. Thermal Stability at 135°C

The thermal stability of our candidate polymers is being determined by isothermal gravimetric analysis. Samples are heated at 135°C in a nitrogen atmosphere for 60 hours. The extent of degradation is determined by measuring weight loss and by comparing the infrared spectra of the polymers before and after exposure.

Table 3 lists data from these tests. It appears that the initial weight losses are due to adsorbed volatiles, principally water, in the samples. Only one polymer, polystyrene-azosalicylic acid, can be considered unstable.

2-Vinylpyridine-methacrylic acid copolymer developed a small adsorption in the infrared at 5.6μ after exposure. This adsorption is characteristic of anhydride groups and indicates that the polymer probably dehydrated slightly under the test conditions. Similar analysis of the ethylene-maleic acid copolymer (EMA-22) indicated that it dehydrated almost quantitatively to its anhydride during the test. No definite changes in polymer structure were detected from infrared spectra of other samples tested.

2. Stability in 40% KOH at 135°C

a. Test Procedure

The following procedure was used to test the stability of our ligand-containing polymers in strong caustic.

(1) Powdered samples of each polymer were immersed in 40% KOH contained in a Teflon lined stainless steel bomb.

(2) The bombs were heated in an oven controlled at 135 ± 1.5°C for at least 60 hours.

(3) The polymer was recovered and examined.

In this test, all material that dissolves in the 40% KOH test solution, both stable but soluble fractions of polymer and soluble degradation products, are considered as weight lost.

Table 3

THERMAL STABILITY OF MODEL POLYMERS AT 135°C IN NITROGEN ATMOSPHERE

Source/Ref.	Polymer	Wt. Loss (%) After x Hrs.		Change in IR Spectra After Exposure	Change in Appearance After Exposure
		24 hours	After ( ) hours		
Gelvatol®1-90	Poly(vinyl alcohol)	1.7	1.7(48)	---	none
Formvar®95-15S	Poly(vinyl formal)	0.63	0.54(69)	Dec. 8-10μ	---
Butvar®-76	Poly(vinylbutyral)	5.63	6.44(95)	Sl. Dec. 12.4μ	Yellowed and fused
89782	Poly(p-aminostyrene)	3.4	3.7(71)	broadened	none
89772	Poly(aminonitrostyrene)	3.2	4.3(95)	none	none
	Poly(styrene azo-salicylic acid)	7.3	8.7(72)	general broadening	---
	Poly(styrene azo-8-hydroxyquinoline)	6.9	7.4(95)	general broadening	---
89932	Polyvinylbenzyl-catechol	0	0 (68)	Sl. Inc. 6.0-6.2μ	Darkened
89775	Poly(vinylbenzyl-salicylic acid)	4.7	5.2(93)	general broadening	none
89789	Poly[N-(2-pyrimidyl)aminostyrene]	7.9	7.9(65)	none	none

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Table 3

THERMAL STABILITY OF MODEL POLYMERS AT 135°C IN NITROGEN ATMOSPHERE

(Continued)

Source/Ref.	Polymer	Wt. Loss (%) After x Hrs. 24 hours	After ( ) hours	Change in IR Spectra After Exposure	Change in Appearance After Exposure
89784	Poly[vinylbenzyl-1-(β-aminoethyl)-2-methyl-2-imidazoline]	0	0(71)	none	none
89754	Polyvinylbenzyl-2-(2-pyridylethyl)amine	2.8	4.3(83)	Sl. Inc. 5.8-6.14μ	Darkened
Monsanto CD-600	Styrene-acrylonitrile-butadiene polymer	0.8	(+0.4)(95)	general broadening	fused, slight yellowing
Lytron®100	Styrene-methyl-acrylate copolymer	1.4	1.7(71)	---	none
Lytron®810	Styrene-maleic anhydride	4.7	4.7(116)	none	---
Monsanto EMA-22	Ethylene-maleic acid copolymer	13.8	13.8(70)	inc. 5.4-5.8, 6.95,7.5μ dec.5.92,7.15μ	none
Monsanto EMA-54	Ethylene-sodium maleate copolymer	4.5	5.1(95)	dec. 5.9μ	none
Gantrez®AN-169	Methylvinylether-maleic anhydride copolymer	5.5	5.5(89)	none	none
Monomer-Polymer Laboratories	Poly-N-vinyl-carbazole	0.33	0.47(72)	---	---

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Table 3

THERMAL STABILITY OF MODEL POLYMERS AT 135°C IN NITROGEN ATMOSPHERE

(Continued)

Source/Ref.	Polymer	Wt. Loss (%) After x Hrs. 24 hours	() hours	Change in IR Spectra After Exposure	Change in Appearance After Exposure
PVP-NP-K30 (General Aniline and Film Corp.)	Poly-N-vinyl-pyrrolidone	6.4	6.6(114)	general broadening	---
B.A.S.F.	Poly(N-vinylimidazole)	5.7	5.7(63)	none	slight yellowing
89929	Polyethyleneimine-N-(5-methylene-8-hydroxyquinoline)	5.5	6.2	Broadened, inc. 6.1-6.2μ	Darkened
89768	2-Vinylpyridine-methacrylic acid copolymer	5.3	5.7(70)	5.6μ appears	---
89771	2-Vinylpyridine-methylacrylate polymer	5.2	3.8(68)	Unchanged	Fused

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The procedure for recovery of the polymers necessarily varied because of the different solubility characteristics of the polymers. The following tabulation illustrates the general procedure used to remove KOH residues from the recovered samples:

	Polymer Type	KOH Removal Method
A.	Water-insoluble	Multiple washing with water
B.	Water-soluble	
	1. Alcohol-insoluble	Multiple washing with alcohol
	2. Alcohol-soluble	Extract with organic solvent and recover by evaporation of solvent
C.	Salt-forming	Neutralize and wash free of salts as for A or B above

The recovered products were checked for possible degradation by comparing weight, appearance, infrared spectra, softening points, solubility characteristics, and viscosity before and after exposure. These data are summarized in Table 4.

b. **Analysis of Polymers Exposed to 40% KOH at 135°C**

1) **Vinylpyridine-(meth)acrylic Acid Copolymers**

Ligand-polymers of this type that were tested were highly resistant to 40% KOH. Weight losses were low and properties of recovered polymers were essentially unchanged. For example, a 0.57:0.43 2-vinylpyridine-methacrylic acid copolymer suffered only 3.2% weight loss and had identical viscosity in 0.45% dimethylformamide solutions before and after exposure.

The 2-vinylpyridine-methyl acrylate copolymer was also recovered essentially unchanged after exposure except for saponification of its ester group. The physical properties of the exposed sample were compared to those of a sample of this copolymer that was saponified in 1N NaOH.

A copolymer of ethyl-2-vinylpyridine-methacrylic acid in ratio 0.58:0.42 showed much higher weight loss (16.5%) than other polymers of this type. This weight loss may be due to loss of low molecular weight soluble portions rather than degradation resulting from the presence of the ethyl group. Properties of recovered polymer were essentially unchanged.

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Table 4

STABILITY OF MODEL POLYMERS IN 40% KOH AT 135°C

Source/Ref.	Polymer	Wt. Loss (%) After 63 Hours	Change in Appearance	Change in IR Spectra	Viscosity Comparison [η]Before	[η]After	Solvent	Softening Point, °C Before	After
89768	2-Vinylpyridine-methacrylic acid	3.2	sl. yellow		1.08*	1.08*	Dimethyl-formamide	215-220	177-185
89771	2-Vinylpyridine-methyl acrylate copolymer	(+4)	-	14.3 appears	0.38	0.41	Dimethyl-formamide	135-247	140-240
89787A	Ethylvinylpyridine-methacrylic acid copolymer	16.5, 13.1	darkened	Dec.6.15µ	1.08*	1.10*	Dimethyl-formamide	195-210	205-220
Monomer-Polymer Laboratories	Poly-N-vinyl-carbazole	2.1	None	Dec.3.48 and 10.4µ	0.61	0.63	Dimethyl-formamide	224-265	223-280
Lustrex®	Polystyrene	1.0	fused	--	0.52	0.57	Benzene	125-135	109-125
Amberlite® 120HCP	Sulfonated polystyrene	(+1.9)	None					over 300	over 300
89782	Poly(p-amino-styrene)	2.8	None	None				230 to over 300	230 to over 300
89752	Polyvinylbenzyl-chloride	0.6	-	None	insoluble after test			245-	245-
89777	Poly[vinylbenzyl-1-(2-pyridylmethylamine)]	3.6	None	None	-	-	-	over 300	over 300
89784	Poly[vinylbenzyl-1-(β-aminoethyl)-2-methyl-2-imidazoline]	4.1	None	None	-	-	-	over 300	over 300
89932	Polyvinylbenzyl-catechol	10.0	Darkened	inc.6.0-6.2µ	-	-	-	over 300	over 300
89754	Polyvinylbenzyl-2-(2-pyridylethyl)amine	9.7	Darkened	5.9-6.1 inc.	-	-	-	over 300	over 300

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Table 4

STABILITY OF MODEL POLYMERS IN 40% KOH AT 135°C

(Continued)

Source/Ref.	Polymer	Wt. Loss (%) After 63 Hours	Change in Appearance	Change in IR Spectra	Viscosity Comparison [η] Before	[η] After	Solvent	Softening Point, °C Before	After
89775	Poly(vinylbenzyl)-salicylic acid)	16.2	None	Inc. 6.68 Dec. 6.0,8.95, 11.45				over 300	over 300
89929W	Polyethyleneimine-N-(5-methylene-8-hydroxyquinoline)	3.3	None	Inc. 6.1,7.15μ broadening				140-	160-240
CN-54 Monsanto	Styrene-acrylonitrile copolymer	9.4	fused	inc. 6.1-6.2μ	1.49*	1.48*	Dimethyl formamide	120-220	125-205
CD-600 Monsanto	Stryene-acrylonitrile butadiene polymer	25.5	darkened and fused (NH_3 odor in KOH)	very minor	1.30*	1.28*	Dimethyl-formamide	120-220	117-205
Lytron® 810	Styrene-maleic anhydride copolymer	up to 21	darkened	None	1.83**	1.56**	Dimethyl-formamide	235-288	230-285
PVP NK-30	Poly-N-vinyl-pyrrolidone	16.0	darkened & hardened	general broadening	insoluble after test			180-210	208-275
FORMVAR® 95-15S	Poly(vinylformal)	20.8	darkened & hardened	5.8 gone; 8.1 dec.; 6.2 - 6.5μ inc.	insoluble after test			145-210	over 300
Butvar® 76	Poly(vinylbutyral)	19.5	hardened	broadened	insoluble after test			80-200	95-185
Butvar® 72 A	Poly(vinylbutyral)	22.3	hardened	Hydroxyl, 7.0, 7.5, 8.1 dec: 6.45μ appears	insoluble after test			95-215	175-over 300
Gelvatol® 1-90	Poly(vinyl alcohol)	47.3	colored black	6.5, 7.3μ appears	1.09	only 12% of recovered solid was soluble	H_2O	225-230	over 300

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Table 4

STABILITY OF MODEL POLYMERS IN 40% KOH AT 135°C

(Continued)

Source/Ref.	Polymer	Wt. Loss (%) After 63 Hours	Change in Appearance	Change in IR Spectra	Viscosity Comparison [n]Before [n]After Solvent			Softening Point, °C Before	After
89772	Poly(aminonitro-styrene)	28.3	darkened	broadened; 7.5μ dec.	--		--	--	--
	Poly(styrene-azo-salicylic acid)	23.9ττ		broadened	insoluble polymer			over 300	--
	Poly(styrene-azo-8-hydroxyquinoline)	25.3τττ		inc. 6.2, 7.5μ dec. 6.7, 7.3, and 8.2μ	insoluble polymer			over 300	--
BASF	Poly(vinylimidazole)	39.7, 40.3	became black	none	insoluble after exposure			210-300	over 300
EMA® 22	Ethylene-maleic acid copolymer		soluble in 40% KOH						
Gantrez® AN-169	Methylvinylether-maleic anhydride copolymer	(100)	soluble in 40% KOH	--	--	--	--	--	--

τ   Comparisons made with acid form of hydrolyzed polymers
*   Relative viscosity at 0.5% concentration. All viscosities were measured at 30°C
** Relative viscosity of acid form at 0.15%
ττ Loss after exposure for 63 hours longer was 20.2%
τττ Loss after exposure for 63 hours longer was 18.9%

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2) <u>Candidate Polymer Backbones</u>

Polystyrene and poly-N-vinylcarbazole were recovered essentially unchanged after exposure.

3) <u>Polystyrenes with Ligands on Methylene Linkage</u>

The methylene linkage on polystyrene was found to be stable under test conditions. Therefore, screening tests of polystyrenes containing ligand substituents on a methylene linkage appears to measure the stability of the ligand substituent itself. The stability of the methylene linkage was confirmed by almost quantitative recovery of polyvinylbenzylchloride after exposure. This polymer crosslinked slightly during exposure since the exposed sample was insoluble in dioxane and other solvents for the linear polymer. However, the infrared spectrum of the exposed sample showed that the major part of the chloromethyl groups was still present (7.96 μ).

The fact that this chloromethyl group was not hydrolyzed under test conditions is surprising. However, analysis of degradation products of polymers tested so far point up the fact that 40% KOH acts principally as a dehydration agent. Only very reactive groups such as esters and anhydrides hydrolyze in 40% KOH under the test conditions.

Several polymers that have methylene linkages between the ligand groups and the polymer backbone were tested. Two of these, poly[vinylbenzyl-1-(2-pyridylmethylamine)] and poly[vinyl-benzyl-1-(β-aminoethyl)-2-methyl-2 imidazoline], were recovered essentially unchanged after the test.

Two other polyvinylbenzyl polymers tested had slightly higher weight losses. These polymers had catechol and 2-(pyridylethyl) amine as ligand substituents and lost about 10% weight on exposure. Changes in structure of recovered polymers detected in the infrared spectra were minor. Both polymers showed increase in absorption at 6 ± 0.2μ, some of which may be caused by differing amounts of adsorbed water on these hydroscopic polymers. Quinone formation from air oxidation is a possible source of these absorptions in the catechol polymer.

Another polymer of this type, poly(vinylbenzylsalicylic acid), had a weight loss of 16%. Changes detected in its infrared spectra indicate this weight loss may be due to decarboxylation.

4) Other Substituents on Polystyrene Backbone

Poly(aminostyrene) and poly(aminonitrostyrene) were tested since unreacted amino and nitro groups are present in some polymers derived from poly(aminostyrene). Poly(aminostyrene) was stable and was recovered unchanged. The poly(aminonitrostyrene) sample, however, was degraded extensively. This sample showed no adsorption in the infrared at 7.5μ characteristic of the nitro group after exposure. The weight lost (28%) by the sample is equivalent to loss of the nitro substituent from the polymer, but degradation was probably a complicated process involving partial reduction of the nitro group and oxidation of the polymer. The dark red coloration of the KOH solution, visible after the test, indicates the probable presence of partially reduced ionized nitrogen species (ref. 10). These results indicate that it is necessary to use poly(aminostyrene) free of all nitro groups in polymer preparations to insure stability, but unreacted amino groups can be tolerated.

Two polymers with the azo linkage on polystyrene backbones were tested: polystyrene-azo-8-hydroxyquinoline and polystyrene-azosalicylic acid. Both polymers lost approximately 25% of their weight during 63 hours' exposure. The same samples when exposed to a second 63-hour cycle continued to lose weight at approximately the same rate. The low stability of these polymers may be caused, in part, by the presence of nitro substituent impurities.

The sulfonic group on the polystyrene backbone appears to have good stability in 40% KOH. A sample of Amberlite 120 HCP was recovered without loss of weight.

5) Polymers Containing Acrylonitrile

Acrylonitrile is potentially a useful monomer for this program because of its ability to copolymerize with some monomer-ligands that do not homopolymerize. Two polymers containing acrylonitrile, a styrene-acrylonitrile copolymer (Monsanto CN-54) and a styrene-acrylonitrile-butadiene terpolymer (Monsanto CD-600), were tested. Comparison of the infrared spectra of exposed and fresh samples indicated that most of the nitrile substituent survived unchanged. Comparison of viscosity of polymer solutions and softening points of these polymers before and after also indicated little attack by KOH. Slight hydrolysis of the terpolymer did occur; the odor of ammonia was evident in the sample after exposure. However, the extent of hydrolysis of both these samples was very minor compared to that reported for the homopolymer, polyacrylonitrile. For example, Kern and Fernow (ref. 11) report hydrolysis in warm 40% NaOH of

poly(acrylonitrile) is essentially quantitative. The lower
stability of the homopolymer may be the result of the greater
solubility of its hydrolysis product, poly(sodium acrylate), in
40% caustic.

In conclusion, these test results indicate that the physical
properties of separator materials would probably not be effected
adversely by the sterilization cycle. However, these materials
probably could not be used as separator materials because of the
detrimental effect of even small amounts of ammonia on the
silver oxide electrode.

6) Maleic Anhydride Copolymers

The recovered, exposed samples of a styrene-maleic anhydride
copolymer had almost identical properties to a sample hydrolyzed
in 1N NaOH except viscosity was slightly lower. The difficulty
in recovering these water-soluble polymers limited accuracy in
measuring weight loss. Weight loss of an exposed sample recovered
by acidification and washing with dilute HCl was 21.5% compared
to 23% for a control sample hydrolyzed in 1N NaOH and recovered
in the same way.

Samples of ethylene-maleic acid copolymer (EMA-22) and
methylvinylether-maleic anhydride copolymer (Gantrez AN-169)
were found to be soluble in 40% KOH.

7) Poly(vinylacetals) Derived from Poly(vinyl alcohol)

The acetal group itself,

$$\left[\begin{array}{c} CH-CH_2-CH-CH_2- \\ O \qquad\qquad O \\ \diagdown \qquad \diagup \\ CH \\ | \\ R \end{array} \right]_n$$
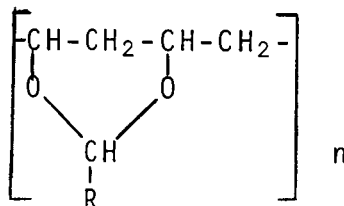
appears stable under the test conditions. However, stability
of the acetal polymer appears to be limited by degradation of
unreacted hydroxyl groups on these polymers. These conclusions
are based on the following evidence:

1. The magnitude of absorptions in the infrared,
    attributed to formal and acetal functions
    (ref. 12), are approximately the same in the
    samples before and after the exposure period,
    although exposed samples show general broadening

in these regions. (Disappearance of acetate
function is detected in these spectra).

2. Weight loss of all acetal polymers was appreciably
   less than weight loss by polyvinyl alcohol.
   Degradation of polyvinyl alcohol was extensive as
   shown by a weight loss of 47% and the fact that
   the recovered product was largely insoluble in
   water indicating extensive crosslinking.

3. Weight loss by acetals with different substi-
   tuents but identical acetal functionality were
   about the same.

In conventional methods of preparing acetal polymers the
highest acetal functionality obtained is 80-88%. Therefore,
this class of compounds was dropped from consideration.

8) Poly-N-vinylpyrrolidone

In the test in 40% KOH this polymer degraded to an insoluble,
presumably crosslinked product with 16% loss of weight. Its
spectra in the infrared was unchanged after exposure except for
a general broadening. In 1N NaOH the pyrrolidone ring is
reported to open to form an amino acid and the polymer remains
soluble (ref. 13).

9) Poly(N-vinylimidazole)

A sample of this polymer supplied by Badische Anilin and
Soda-Fabrik AG lost 39% of its weight during exposure in 40%
KOH at 135°C. The recovered fraction apparently was highly
crosslinked since its softening point was higher than the fresh
sample, and it was no longer soluble in water. Its spectrum in
the infrared was unchanged, however.

C. ELECTRICAL RESISTANCE OF MEMBRANES

Our apparatus for testing electrical resistance of the
membranes has been assembled and initial tests are being made.
The general procedure described by Salkind and Kelley (ref. 14)
for measuring electrical resistance in 40% KOH is being followed.
Measurements are made with a Wayne-Kerr Component Bridge,
Model B522. The resistance cell is essentially as described in
reference 14 but includes the latest improvements made by the
ESB personnel. Measurements are made on membranes after soaking

overnight in 40% KOH. Values obtained for membranes cast from solutions of the respective polymers are listed in Table 5. Values of ρ reported here are subject to some error since film thickness tolerances were 2 to 3 mils in most cases.

Table 5

ELECTRICAL RESISTANCE OF MEMBRANES IN 40% KOH

No.	Polymer	Film Thickness in	Measured Resistance* ohms	Area Resistance ohm in^2	Resistivity,ρ ohm-cm
1	Poly(vinyl alcohol)	0.006	0.722	0.022	9.4
2	Styrene-maleic anhydride	0.005	0.775	0.028	14.1
3	2-Vinylpyridine-methyl acrylate	0.005	350		
3'	3 after 16 hours at 95°C in 40% KOH		330		
3"	3 after 16 hours at 135°C in 40% KOH	0.039	8.1	0.83	54
3"'	Sample No. 2 of polymer 3 after 14 hours in 40% KOH at 135°C	0.008	5.87	0.58	182
4	Poly(vinylimidazole)	0.020	118	13	1650

*Includes a cell resistance without membrane of 0.522 ohms.

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IV. PROGRAM PLAN

A. GENERAL

The overall approach to be followed in accomplishing our contract objectives can be divided into the following four phases:

1. Preparation of ligand-containing polymers.

2. Screening tests

3. Preparation of copolymers and membranes.

4. Comprehensive tests

Our long-range program planning chart showing the proposed distribution of effort to be expended on each of these phases is given in Table 6.

B. ANTICIPATED WORK FOR NEXT QUARTER

1. Develop polymer systems containing 2-vinylpyridine-acrylic acid and 2-vinylpyridine-methacrylic acid units with improved film-forming ability.

2. Start comprehensive evaluation of these and other polymers that showed promise in the screening tests.

3. Continue to screen new candidate polymers for thermal stability at 135°C and for stability in 40% KOH at 135°C.

Table 6

OVERALL PROGRAM PLANNING CHART

Per cent of Total Research Effort

Program Phase	May	June	July	Aug	Sept	Oct	Nov	Dec	Jan	Feb
1. Preparation of ligand containing polymers	80	80	80	40	20	20	20	-	-	-
2. Screening tests	20	20	20	20	10	10	10	10	10	
3. Preparation of co-polymers and membranes				40	40	40	40	50	60	10
4. Comprehensive tests					30	30	30	40	30	50
5. Final report										40

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